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(54) PROCESS FOR THE PREPARATION OF MONOHALOGENALKENES, CATALYST THEREFOR AND PROCESS FOR THE PREPARATION THEREOF

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention is concerned with a process for the preparation of monohalogenalkenes by halogenating an alkene in the gaseous phase in the presence of a catalyst. The invention is also concerned with a catalyst suitable for use in the aforementioned process and with a process for the preparation of such catalyst.

As used herein the terms "halogenation" and "halogenating" relate to a halogenation reaction effected in the presence of hydrogen halide and molecular oxygen. The hydrogen halide may be added as such to the zone in which the halogenation reaction is effected and/or may have been formed in situ during the halogenation reaction, for example by use of a gaseous mixture comprising gaseous halogen and/or organic halide.

A process of the aforementioned type is known from U.K. Specification No. 1062171 which refers to catalysts comprising compounds of palladium, of copper and of rare earth metal supported on a carrier material. In Example X of said Specification there is used a catalyst which contains cerium and palladium and copper in a palladium: copper atomic ratio of 1:8.4. Use of this catalyst in the chlorination of propene at a temperature of at least 370° C yielded allyl chloride at a selectivity of 42% and isopropyl chloride at a selectivity of 29%.

It has been found that the halogenation of alkenes can be effected with better results when use is made of catalysts of this general type in which the palladium to copper atomic ratio is in a particular range.

The invention is concerned with a process for the preparation of a monohalogenalkene which comprises contacting, in the gaseous phase and under halogenation reaction conditions, an alkene with a hydrogen halide and molecular oxygen in the presence of a halogenation catalyst comprising:

(a) at least one compound of palladium and at least one compound of copper in a palladium: copper atomic ratio of between 1:0.1 and 1:1.5, (b) at least one compound of at least one element selected from yttrium, scandium and the rare earth metals, as herein defined, (c) at least one compound of at least one alkali metal in an alkali metal: copper atomic ratio of between 1:0.1 and 1:4, and (d) carrier material.

The invention also is concerned with such a catalyst.

It has been found that the use of a catalyst wherein the palladium: copper atomic ratio lies within the above-mentioned range provides excellent selectivity to monohalogenalkene at a relatively good alkene conversion. By selectivity to monohalogenalkene is meant the ratio, expressed as a percentage, of the number of moles of alkene converted to monohalogenalkene to the total number of moles of alkene reacted. Such selectivity can be obtained at relatively low temperatures, as a result of which less corrosion is encountered in the equipment used, less carbon is deposited on the catalyst (and thus the life of the catalyst is longer) and less copper is lost by evaporation. The palladium: copper atomic ratio pre-

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ferably is between 1:0.8 and 1:1.2 and more preferably is about 1:1.

As used herein the term "rare earth metals" is defined to include the 15 elements with atomic numbers 57 to 71 inclusive.

As far as the choice of yttrium, scandium and the rare earth metals is concerned, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium are preferred. Very good results are obtained with a mixture known as "didymium". The term "didymium" is sometimes used to indicate a mixture containing rare earth metals other than cerium in a ratio occurring in nature. This definition agrees with that given in Kirk-Othmer, "Encyclopaedia of Chemical Technology", Second Edition, Volume 4, page 843. However, in this specification the term "didymium" is used in a wider sense, namely to indicate any mixture containing rare earth metals in a ratio occurring in nature. These mixtures may therefore be rich or poor in cerium. In some types of "didymium", lanthanum and neodymium are the most frequently occurring rare earth metals although small quantities of praseodymium and samarium also may be present. In other types of "didymium", neodium and samarium are the most frequently occurring rare earth metals although small quantities of praseodymium and gadolinium also may be present. A typical example of "didymium" analyses in weight percent as La_2O_3 43%, Nd_2O_3 36%, Pr_2O_{11} 11%, Sm_2O_3 5%, Ce_2O_3 2%, Gd_2O_3 2% and Y_2O_3 1%.

As far as the choice of alkali metals is concerned, lithium, sodium and potassium are preferred, lithium and potassium being most preferred. Use of catalysts containing potassium compounds provides high yields of monohalogenalkene while use of catalysts containing lithium compounds provides excellent selectivity in monohalogenalkene.

The atomic ratio of the element or elements of yttrium, scandium or the "rare earth metals" to copper in the catalyst may vary between wide limits determined, on the one hand, by the minimum quantity of yttrium, scandium or rare earth metal which provides an increase in the yield of monohalogenalkene and, on the other hand, that quantity of yttrium, scandium or rare earth metal above which no increase in the yield of monohalogenalkene results. The yttrium, scandium or rare earth metal and the copper preferably are present in the catalyst in amounts to provide a yttrium, scandium or rare earth metal:copper atomic ratio of between 1:0.25 and 1:4.

The palladium content of the catalysts may vary between wide limits determined, on the one hand, by the minimum quantity of palladium which provides catalytic activity and, on the other hand, by the maximum quantity of palladium which the carrier material can support, said maximum quantity depending, inter-

alia, on the specific surface area and the pore volume of the carrier material. The catalyst contains preferably between 10 and 200, more preferably between 25 and 100, milligram-atoms of palladium per litre of carrier material.

The specific surface area and the specific pore volume of the carrier material are not of critical importance. However, catalysts comprising carrier materials having a relatively large surface area, for example 300 m^2/g , have a relatively short life. Therefore preference is given to the use of carrier materials having a specific surface area not greater than 50 m^2/g since catalysts comprising such material have a relatively long life.

The carrier material must resist attack under the conditions prevailing during the halogenation of the alkene. Examples of suitable carrier materials are alpha-alumina, silica, ceramic materials, pumice, diatomaceous earth, titanium oxide and zirconium oxide. Mixtures of carrier materials may be used. Preference is given to alpha-alumina and silica.

The metal compounds (a), (b) and (c) are preferably halides corresponding to the halogen of the hydrogen halide used. The present process is suitable for the chlorination and bromination of alkenes and is particularly suitable for the chlorination of alkenes.

Examples of alkenes which may be halogenated are ethene, propene, 1-butene, 2-butene, isobutene, branched and unbranched pentenes, hexenes, octenes, nonenes and decenes; oligomers of lower olefins, for example trimers and tetramers of propene, dimers and trimers of isobutene; cyclic alkenes, for example cyclopentene and cyclohexene; and substituted alkenes containing aryl groups, for example styrene. Mixtures of alkenes can be employed.

The temperature at which the process is carried out depends, amongst other things, on the alkene and hydrogen halide used. As stated hereinbefore, relatively low temperatures can be employed. The chlorination of propene at a temperature of between 230 and 280°C produces a relatively high yield of allyl chloride. If desired, however, chlorination of propene may be conducted at a temperature below 230°C or above 280°C.

The space velocity of the gases contacting the catalyst is not critical; it is preferred that the contacting is carried out at a space velocity such that between 25 and 2,000 litres (calculated at S.T.P.) of alkene, hydrogen halide and molecular oxygen contact each litre of catalyst per hour.

Suitable ratios for the various components of the gaseous mixture which participate in the reaction may easily be determined by experiment. As a rule, it is recommended that the ratio of alkene to chlorine (free and bound) in the reaction mixture be chosen to provide from 0.25 to 2 gram-atoms of chlorine per

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mole of alkene. The conversion of alkene is optimum when from 0.5 to 1.2 gram-atoms of chlorine are provided per mole of alkene. It is recommended that the proportion of oxygen 5 in the reaction mixture be adjusted so that a good yield of monohalogenalkene is produced. In general, it is further recommended that the gaseous mixture contains at least 0.25 but not more than 2 moles of oxygen per gram- 10 atom of chlorine.

The halogenation can be carried out in the presence of a gaseous diluent, for example selected from nitrogen and carbon dioxide.

The catalyst may be used in any suitable 15 manner, for example in the form of a fixed, moving or fluidized bed. The use of a fluidized bed is preferred since the temperature of the bed can readily be controlled.

The pressure during the halogenation reaction 20 can vary between wide limits. Pressures of between 0.1 and 100 atm are recommended; pressures between 0.5 and 50 atm are preferred and between 0.9 and 10 atm are most preferred.

The monohalogenalkene can be removed 25 from the reaction mixture in any suitable manner. Considering the preparation of allyl chloride from propene, hydrogen halide and oxygen when, in addition to allyl chloride, isopropyl chloride, dichloropropanes, dichloro- 30 propenes, trichloropropanes and oxidation products may be formed, the reaction mixture may be cooled to ambient temperature and subsequently separated into a gas phase and a 35 liquid phase. The gas phase contains unreacted alkene and hydrogen halide and the liquid phase comprises an aqueous phase and a chlorinated hydrocarbon phase. After separation of the components of the liquid phases, 40 allyl chloride can be obtained from the chlorinated hydrocarbon phase by distillation.

Monohalogenalkenes obtained by the process according to the present invention have various uses depending on the structure thereof. For example, allyl chloride can be employed 45 in the preparation of (a) epichlorohydrin, from which epoxy resins and glycerol can be synthesized, (b) 1,2 - dibromo - 3 - chloropropane, which is used in agriculture as a vermicide, 50 and (c) allyl alcohol, which is a starting material for the preparation of synthetic resins, perfumes and pharmaceutical products. Esters of allyl alcohol are very suitable for use as intermediate products in the preparation of 55 polymerization products; important esters are the carbonate esters and the diallyl esters of dibasic acids, for instance phthalic acid.

The invention also is concerned with a process for the preparation of a catalyst as hereinbefore defined comprising applying to carrier material (a) at least one compound of palladium and at least one compound of copper in a palladium:copper atomic ratio of between 1:0.1 and 1:1.5, (b) at least one compound

of at least one element selected from yttrium, scandium and the rare earth metals, as herein defined, and (c) at least one compound of at least one alkali metal in an alkali metal:copper atomic ratio of between 1:0.1 and 1:4. 65

The sequence in which the compounds of palladium, copper, element(s) selected from yttrium, scandium and rare earth metals and alkali metal are applied to the carrier material may vary in any of the ways possible. For example, the element(s) selected from yttrium, scandium and rare earth metals can be applied to the carrier material before, simultaneously with or after the application thereto of palladium, copper and the alkali metal. Alternatively, it is possible to apply first palladium, then copper, subsequently the element(s) selected from yttrium, scandium and the rare earth metals and finally the alkali metal. 70

The application of the various catalytic components to the carrier material may be effected in any suitable way. For example, the carrier material may be impregnated with an aqueous solution of a metal compound to provide impregnated carrier material which is dried and then subjected to a heat treatment. Impregnation may be effected in several steps using solutions having equal or differing concentrations of catalytic material. The various components can be applied to the carrier material directly as halides or in the form of compounds which as a result of treatment with hydrogen halide, if required in the presence of elemental oxygen, are converted into halides. Examples of the latter group of compounds are oxides, hydroxides, carbamates, acetates and nitrates. 75

The heat treatment suitably may be effected at a temperature of between 200 and 500° C for a period of from 1 to 10 hours. If desired, however, shorter or longer periods and/or lower or higher temperatures may be employed. The heat treatment is usually carried out in the presence of air. If so desired, the heat treatment may be conducted in a plurality of steps under different conditions, optionally with intermediate addition of any of the catalytic components to the carrier material. It is recommended that, after the last such addition, hydrogen halide and/or halogen be passed over the catalyst at elevated temperature in order to convert the catalytic components into halides. Such a treatment usually is effected at a temperature of between 100 and 500° C. However, particular preference is given to the use of a temperature of from 300 to 400° C in this treatment. 80

The invention is illustrated by the following Examples; as used in the Tables, the term "selectivity" is the ratio, expressed as a percentage, of the moles of propene converted to the specified product to the total moles of propene reacted and "mat/l" is an abbreviation for milligram-atoms per litre. 85

EXAMPLE I.
Preparation of the catalysts used in Examples II to V

Alpha-alumina having a specific surface area of less than 5 m²/g and a pore volume of 0.22 ml/g was extracted at room temperature successively with 2 N hydrochloric acid and water and then dried for two hours at 300° C in air. The dried alumina contained 60 milligram-atoms (mat) of sodium per litre of alumina. The dried alumina was impregnated with a 2 N hydrochloric acid solution containing the catalyst components in the form of chlorides, the quantity thereof being the maximum that could be taken up by the alumina. The impregnated alumina was stirred for some time and then dried for 2 hours at 300° C in air. Subsequently, a gaseous mixture comprising 2 volume parts of hydrogen chloride and 1 volume part of oxygen was passed over the resulting catalyst for 1 hour at 360° C and atmospheric pressure. The prepared catalyst had a bulk density of 1.12 g/ml.

Didymium trichloride was used as the source of the rare earth metal compound. This trichloride contained (expressed in weight percent metal calculated on didymium trichloride trihydrate) gadolinium 1.2, neodymium 18, yttrium 1.5, cerium 13, lanthanum 3.7, praseodymium 4.1 and samarium 2.5.

EXAMPLE II.
A gaseous mixture comprising propene, hydrogen chloride and air in a propene:hydrogen chloride: oxygen molar ratio of 1:1:0.48 was passed through a fluidized bed of catalyst at 275° C and atmospheric pressure. The space velocity, expressed as litres of gaseous mixture at STP per litre of catalyst per hour was 440. After the gaseous mixture had been passed through the catalyst for 8 hours, the reaction mixture was analysed. Two different catalysts were tested. The results are presented in Table I.

TABLE I

Test No.	Composition of catalyst, mat/l of carrier material				Conversion of propanes, mole %	Yield of allyl chloride, mole %	Selectivity, mole %, towards isopropyl-dichloro-chloride + 1-chloro-propene	Oxidation products
	Pd	Cu	Di	Li				
1	50	100	25	200	9.4	3.8	40.0	16
2	50	50	25	200	8.6	5.9	68.7	15.6

* not according to the invention.

Comparison of the results of the two tests shows a notable increase in selectivity to and yield of allyl chloride when a catalyst having a Pd:Cu atomic ratio of 1:1 was used compared to when a catalyst having a Pd:Cu atomic ratio of 1:2 was used.

TABLE II

Time of analysis of reaction mixture after initiation of reaction (hours)	Conversion of propene, mole %	allyl chloride	Selectivity, mole %, towards		
			isopropyl chloride + 1-chloro-propene	dichloropropanes + dichloropropenes	oxidation products
2	14.0	69.8	24.7	<1	5.4
8	13.1	72.7	21.9	0.4	4.9
26	12.2	70.0	24.5	<1	5.0
52	9.8	67.5	27.0	<1	5.0
77	8.8	63.0	31.8	<1	5.0
114	8.8	63.0	31.8	<1	5.0

From the results reported in Table II it appears that during the first 77 hours of the reaction the conversion of propene and the selectivity to allyl chloride decrease somewhat and then remain constant for at least a further 37 hours.

Test 2 of Example II was repeated at a temperature of 250° C and a space velocity of 88 (litres of gaseous mixture of STP per litre of catalyst per hour). The results are presented in Table II.

TABLE III

Time of analysis of reaction mixture after initiation of reaction (hours)	Conversion of propene, mole %	allyl chloride	Selectivity, mole %, towards	
			dichloropropanes + dichloropropenes	oxidation products
485	9.2	83	8	9
1303	8.8	79	2	20
1327	8.7	78	2	20
1502	8.9	79	2	19

Between hours 1285 and 1328, isopropyl chloride was added to the feed in an amount to provide 26 mole % of the feed (calculated on propene) between hours 1285 and 1304 and 14 mole % of the feed (calculated on propene) between hours 1304 and 1328. After 1328 hours the addition of isopropyl chloride was discontinued. The conversion of propene and the selectivities to the various products shown are virtually unaffected by the addition of isopropyl chloride.

hydrogen chloride:oxygen molar ratio of 1:1:0.48 was passed through a fluidized bed of catalyst at a space velocity of 88 (litres of gaseous mixture at STP per litre of catalyst per hour). The catalyst contained (expressed as milligram-atoms per litre of catalyst) 50 Pd, 50 Cu, 25 Di and 200 lithium. The reaction temperature at the start of the test was 250° C and during the test period the temperature was increased three times. From the results presented in Table IV it appears that the highest selectivity to allyl chloride plus isopropyl chloride is obtained when the reaction temperature is between 250 and 270° C.

EXAMPLE V.

A gaseous mixture comprising propene, hydrogen chloride and air in a propane:

TABLE IV

Time after initiation of reaction (hours)	Temperature, °C	Conversion of propene, mole %	Selectivity towards allyl chloride + isopropyl chloride, mole %
40	250	11	94
450	260	12	92
600	270	12	89
650	280	16	80
800	260	12	90

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EXAMPLE VI.

Eight catalysts were tested under the condition described in Example II. The carrier

material of the catalysts was sodium-free except for the catalyst used in Test 3. The results are presented in Table V.

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TABLE V

Test No.	Catalyst composition, mat/l of carrier material					Conversion of propene, mole %	Yield of allyl chloride, mole %	Selectivity, mole %, towards					
	Pd	Cu	Di	K	Na	Li		allyl-chloride	isopropyl chloride	1-chloro-propene	1,2-dichloro-propane	dichloro-propenes	oxidation products
1*	50	50	22.5	—	—	—	5.7	4.1	72	13	2	7	—
2	50	50	22.5	50	—	—	33	17.2	52	6	7	23	10
3	50	50	22.5	—	50	—	20	9.0	45	7	9	27	9
4	50	50	22.5	—	—	50	4.8	3.6	75	19	2	—	—
5	12.5	12.5	5.5	12.5	—	—	9	5.6	62	16	4	16	—
6	87.5	87.5	39.0	87.5	—	—	43	22	51	5	9	19	12
7	87.5	12.5	5.5	12.5	—	—	11	5.5	50	12	6	29	2
8*	12.5	87.5	39.0	87.5	—	—	61	7.3	12	5	6	62	12

* not according to the invention.

Comparison of the yields of allyl chloride of Tests 1, 2 and 3 shows the beneficial influence on the yield of allyl chloride of the use of a catalyst containing potassium or sodium.

5 Comparison of the selectivity to allyl chloride plus isopropyl chloride of Tests 1 to 4 demonstrates the beneficial influence of the use of a catalyst containing lithium. This is important, since isopropyl chloride upon being recycled to the process is converted into allyl chloride.

10 Comparison of Tests 2, 5 and 6 reveals that the yield of allyl chloride is proportional to the amount of catalytic material supported on the carrier material.

15 Comparison of Tests 5 and 7 shows the beneficial influence on the selectivity to allyl chloride plus isopropyl chloride of the use of a catalyst having a Pd:Cu atomic ratio of 1:1 compared to the use of a catalyst having a Pd:Cu atomic ratio of 7:1.

20 Test 8 was carried out using a potassium-

containing catalyst, the composition of which lay outside the scope of the present invention. In this test a very low selectivity to allyl chloride was obtained.

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EXAMPLE VII.

A gaseous mixture consisting of propane, hydrogen chloride and air in a propane:hydrogen chloride: oxygen molar ratio of 1:1:0.48 was passed through a fluidized bed of catalyst at 275° C. The catalyst carrier material was silica having a specific surface area of 23 m²/g and a pore volume of 1.05 ml/g and a sodium content of 5 mmol/l. The space velocity, expressed as litres of gaseous mixture at STP per litre of catalyst per hour was 440. After the gaseous mixture had been passed through the catalyst for 8 hours, the reaction mixture was analysed. Four catalysts were tested. The results are presented in Table VI.

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TABLE VI

Test No.	Catalyst composition, mol/l of carrier material				Conversion of propene, mole %	Yield of allyl chloride, mole %	allyl-chloride propene	Selectivity, mole %, towards		
	Pd	Cu	Di	K				isopropyl-chloride + 1-chloro-dichloro-propenes + oxidation products	dichloro-propanes + dichloro-propenes	
1*	50	100	22.5	50	0	54	14	26	11	56
2	50	50	22.5	50	0	44	21	47	11	37
3*	50	50	22.5	0	0	3	0.4	12	83	<1
4	50	50	22.5	0	200	6	4.3	75	14	<1
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* not according to the invention.

Comparison of the results of Tests 1 and 2 shows the increase in selectivity to and yield of allyl chloride which results when catalyst having a Pd:Cu atomic ratio of 1:1 was used compared to when catalyst having a Pd:Cu atomic ratio of 1:2 was used.

Comparison of the selectivity to allyl chloride obtained in Test 3 and in Tests 2 and

4 shows the necessity for the catalyst to contain alkali metal.

EXAMPLE VIII.
The tests described in Example VII were repeated with three further catalysts. The results are presented in Table VII.

TABLE VII

Test No.	Catalyst composition mat/l of carrier				Conversion of propene mole %	Yield of allyl chloride mole %	Selectivity, mole %, towards		
	Pd	Cu	Di	K			isopropyl- chloride + 1-chloro- propene	dichloro- propanes + 1-dichloro- propene	oxidation products
1	12.5	12.5	5.5	6.0	100	20	9	44	16
2	25.0	25.0	11.0	12.5	200	24	12	49	26
3	50.0	50.0	22.5	25.0	200	31	16	51	21

WHAT WE CLAIM IS:—

1. A process for the preparation of a mono-halogenalkene which comprises contacting, in the gaseous phase and under halogenation reaction conditions, an alkene with a hydrogen halide and molecular oxygen in the presence of an halogenation catalyst comprising:

- 5 (a) at least one compound of palladium and at least one compound of copper in a palladium:copper atomic ratio of between 1:0.1 and 1:1.5,
- (b) at least one compound of at least one element selected from yttrium, scandium and the rare earth metals, as herein defined,
- 15 (c) at least one compound of at least one alkali metal in an alkali metal:copper atomic ratio of between 1:0.1 and 1:4, and
- 20 (d) carrier material.

2. A process as claimed in claim 1, wherein the palladium:copper atomic ratio is between 1:0.8 and 1:1.2.

3. A process as claimed in claim 2, wherein the palladium:copper atomic ratio is about 1:1.

4. A process as claimed in any one of the preceding claims, wherein the yttrium, scandium or rare earth metal:copper atomic ratio is between 1:0.25 and 1:4.

5. A process as claimed in any one of the preceding claims, wherein the rare earth metal is constituted by that mixture of rare earth metals known as "didymium", as herein disclosed.

6. A process as claimed in any one of the preceding claims, wherein the alkali metal is lithium.

7. A process as claimed in any one of claims 1 to 5, wherein the alkali metal is potassium.

8. A process as claimed in any one of the preceding claims, wherein the catalyst contains between 10 and 200 milligram-atoms of palladium per litre of carrier material.

9. A process as claimed in claim 8, wherein the catalyst contains between 25 and 100 milligram-atoms of palladium per litre of carrier material.

10. A process as claimed in any one of the preceding claims, wherein the surface area of the carrier material is not greater than 50 m²/g.

11. A process as claimed in any of the preceding claims, wherein the carrier material is alpha-alumina.

12. A process as claimed in any one of claims 1 to 10 wherein the carrier material is silica.

13. A process as claimed in any one of the preceding claims, wherein the compounds (a), (b) and (c) are halides corresponding to the halogen of the hydrogen halide.

14. A process as claimed in any one of the preceding claims, wherein the halogen is chlorine.

15. A process as claimed in any one of the preceding claims, wherein the alkene is propene.

16. A process as claimed in claim 14 or claim 15, wherein the contacting is carried out at a temperature of between 230 and 280° C.

17. A process as claimed in any one of claims 14 to 16, wherein the contacting is carried out at a space velocity such that between 25 and 2000 litres (calculated at STP) of alkene, hydrogen halide and molecular oxygen contact each litre of catalyst per hour.

18. A process as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples II to VIII.

19. A monohalogenalkene whenever prepared by a process as claimed in any one of the preceding claims.

20. A catalyst comprising:

- (a) at least one compound of palladium and at least one compound of copper in a palladium:copper atomic ratio of between 1:0.1 and 1:1.5,
- (b) at least one compound of at least one element selected from yttrium, scandium and the rare earth metals, as herein defined,
- (c) at least one compound of at least one alkali metal in an alkali metal:copper atomic ratio of between 1:0.1 and 1:4, and
- (d) carrier material.

21. A process for the preparation of a catalyst as claimed in claim 20 comprising applying to carrier material:

- (a) at least one compound of palladium and at least one compound of copper in a palladium:copper atomic ratio of between 1:0.1 and 1:1.5,
- (b) at least one compound of at least one element selected from yttrium, scandium and the rare earth metals, as herein defined, and
- (c) at least one compound of at least one alkali metal in an alkali metal:copper atomic ratio of between 1:0.1 and 1:4.

22. A process as claimed in claim 21 and substantially as hereinbefore described with reference to Example I.

23. A catalyst whenever obtained by a process as claimed in claim 21 or claim 22.

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